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XVI.

CONTRIBUTIONS FROM THE PHYSICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.

XXX. — BOILING POINTS OF NAPHTHALINE, BENZOPHENONE, AND BENZOL UNDER CONTROLLED PRESSURES, WITH SPECIAL REFERENCE TO THERMOMETRY.

By S. W. Holman and W. H. Gleason.

Presented January 11, 1888.

The employment of the melting and boiling of various substances as a means of testing or of graduating thermometers at temperatures above 100° C. is a practice of long standing, especially among chemists. But it will be readily conceded that the results have been in general but roughly approximate, owing to several causes of error, e. g. imperfect purification of substances, faulty apparatus (permitting under or over heating), incomplete systems of thermometry, and errors in the values assumed as the melting and boiling temperatures, these arising, in turn, from causes similar to those just mentioned.

The value of steam as a means of fixing one point on the thermometric scale comes in part from the facts that water does not change composition on boiling at ordinary pressures; that it can be readily obtained in a state of sufficient purity, so that the temperature of its vapor, or rather of a clean thermometer placed in its vapor, can be relied upon as sensibly reproducible under a given pressure; and that this temperature under more than the ordinary range of atmospheric pressure has been measured (by Regnault and Magnus) with sufficient accuracy for thermometric uses. The primary measurement of temperatures above 100° C. is a process of extrapolation from the ice and steam points, and thus possesses the liability to error common to all extrapolation, the magnitude of the error depending upon the method, instruments, and skill employed. It is obvious, therefore, that, whatever be the system of thermometry, a decided gain in accuracy and convenience would accrue to the art of temperature measurement if by competent investigation other substances could be had which at other temperatures should fulfil the conditions just named as rendering steam so useful.

The investigations in this direction by Prof. J. M. Crafts — in part published [*] — contribute far more than any others to the establishment of such fixed reference temperatures. The results of Mills's [†] measurements of melting points are also important. Independent study of the same substances by various observers is valuable, even when the check results cannot claim all the accuracy of the most elaborate investigations. For it is of material importance to answer in this way for each substance the questions: Is the substance reproducible with sufficient certainty to give wholly independent workers sensibly the same temperature? What is this temperature in absolute degrees (of Thomson scale) as a function of the vapor pressure, errors in thermometric methods being eliminated? Is the substance readily reproducible without great expense?

The following is a brief account of a study of naphthaline, benzophenone, and benzol, undertaken with these points in view, and with special reference to attempting to check the results of Professor Crafts. It is probable that, owing to superior facilities and greater experience, he has obtained results entitled to decidedly greater weight than those which we give. But it is believed that the conditions under which our work was done, and the pains taken in the system of air thermometry, entitle the temperature measurements to consideration.

In designing the apparatus we departed somewhat widely from the published descriptions of Crafts's apparatus in almost all details. Our thermometer contained air dried and freed from CO_2, while Crafts's contained hydrogen; its bulb was large (about 200 cc.); the substances studied were either commercially obtained or prepared by methods differing from those of Crafts; and the vapor pressures were under control by a regulator, and were extended through a greater range. We have since learned from Professor Crafts that the form of gas thermometer whose description had been published was not invariably employed, but that others of various capacities and forms had been used.

The concordance of our results with those of Professor Crafts for naphthaline (p. 246) is certainly as close as could be anticipated, and is within the limits of error in even the most elaborate use of the mercurial thermometer at those temperatures. For benzophenone (p. 247) the accordance is from 0°.3 to 0°.5 C., — a difference possibly arising from errors in thermometry introduced by difficulties met with on our part from somewhat irregular action of the kind of glass which we were forced to employ in our air thermometer bulb, and which rendered the determination of its coefficient of expansion somewhat less satisfactory at this higher temperature than at lower ones. Yet we think the difference too great to be wholly accounted for by thermometric errors.

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[*] Crafts. Bulletin de la Soc. Chim., xxxix. 196, 277 (1883).

[†] Mills. Phil. Mag., (5,) xiv. 1 (1882).

The results of the investigation may be summarized as follows: —

1. *Naphthaline*, $C_{10}H_8$, is readily obtainable in a state of sufficient purity to give a reference temperature exact within 0°.1 C. We have found a preparation melting at 79°.4 to 79°.8 to possess a boiling point within the ordinary range of atmospheric pressure (H), expressible by

$$t^\circ = 218.07 + 0.0625\ (H - 760),$$

where H is the reduced pressure in "normal" millimeters of mercury. Throughout the paper the degrees and pressures may be regarded as "normal," i. e. corresponding to the definitions adopted by the International Committee of Weights and Measures, *Trav. et Mém.*, i. (1881). No reduction for gravity has been made, because the correction at Boston is below the limits of error of this work.

2. *Benzophenone*, $(C_6H_5)_2CO$, is obtainable with some difficulty, and is rather costly. With a melting point of 47°.6 to 48°.0 our determination of the boiling point within the ordinary range of atmospheric pressures is expressible by

$$t^\circ = 305.6 + 0.060\ (H - 760).$$

3. *Benzol*, C_6H_6, is readily obtainable nearly pure. Anhydrous benzol melting at 4°.22 was found to have a boiling point expressible within the ordinary range of atmospheric pressures by

$$t^\circ = 80.19 + 0.0455\ (H - 760).$$

4. The boiling points for pressures down to 80 mm. for naphthaline and benzophenone, and to 360 mm. for benzol, are tabulated on page 247. No attempt has been made to express the vapor pressure as a function of the temperature through these greater ranges by any of the numerous formulæ employed by others for this purpose.

5. We regard the actual errors in the final results for the naphthaline and benzol at the atmospheric pressure as under 0°.1, and that for the benzophenone as under 0°.25. The average deviation of the

single observation from the curves upon which the tabular values were interpolated were: naphthaline 0°.1, benzophenone 0°.3, benzol 0°.06.

6. The device used by us for controlling the pressure is easily adjustable, and sufficiently constant to afford, in connection with the substances which we have investigated, a means of obtaining exactly any desired temperature within the range measured. Thus this or a similar apparatus may serve for testing mercurial thermometers at several points, or for maintaining adjusted and known temperatures for other purposes.

Air Thermometer.

Primary temperature measurements to be reducible to the absolute scale (Thomson's) must be made by a gas thermometer, and the air thermometer is the most available. The Jolly* form, in which the closed and open arms of the manometer are connected by a flexible tube, is the most convenient, and was adopted in this work. The difference of level of the mercury surfaces was, however, measured by a special device. Vertically between the two arms of the mercury column is placed a steel millimeter scale of 1.3 cm. square section, and with straight edges. A T-square with double blade is held by the hand firmly against the scale edge, and the blades, which project across the face of the scale, pass, one behind, the other in front of the mercury column. The square is then slid up or down until the plane of the lower edges of the blades is tangent to the top of the meniscus, just as in setting a barometer vernier. By placing the tubes so that there is a bright light behind them, differences of level of the columns can be read with errors of less than one tenth of a millimeter, the tenths being estimated. The bulb used was about 15 cm. long, 4.5 cm. in diameter, and 0.5 to 1 mm. thick, with a capacity of about 200 cc., and the volume of projecting stem was but 0.64 cc. The glass bulb and tube were continuous over to the three-way cock to which the flexible tube was attached. The glass gauge tubes were about 1 cm. inside diameter. The gauges, scale, etc., were carefully protected from heating, and their temperatures obtained by suitably disposed thermometers. The bulb was filled and emptied many times at 100°. The air was thoroughly dried by calcic chloride, sulphuric acid, and phosphoric anhydride, and its carbon dioxide was removed by sodic hydrate. Two determinations of its coefficient of expansion made one before and one after the measurements on naphthaline, gave 0.00 366 95 and 0.00 366 87, of which the mean, 0.00 366 91, was employed. Other values are: —

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* Pogg. Ann., Jubelband.

Regnault	0.00 366 82
Magnus	367 10
Jolly	367 28
Rowland	367 13
Mean	0.00 367 08

With this mean the above value is in so close accordance as to show that the apparatus and coefficient of expansion of glass used must be sensibly correct. The formulæ used in computing a and temperatures was that given by Rowland.*

The coefficient of expansion of the glass bulb of the air thermometer was obtained by a weight thermometer made from the same piece of tubing. Both bulbs were made of the full diameter of the original tube, and with no further heating than was necessary to close the ends. They were thus both of the same diameter and thickness, and had been subjected to substantially the same treatment. In the computations, the values of the coefficient β_t used for mercury were those of Wüllner's recomputation of Regnault's experiments. Measurements were made in vapor of benzophenone, naphthaline, aniline, and water, a special double-jacketed heater being employed. The results were: —

Temp. °	β_t used. (Wüllner.)	κ obtained.
306	0.00 018 667	0.00 003 004
306	667	3 012
218	468	2 895
184	401	2 830
100	253	2 700

The values of κ used for the benzol measurements were determined by Mr. W. S. Hadaway, Jr., on glass of the same kind, at temperatures below 100°. The results overlap at 100°, and are sensibly in accord. In some preliminary work, with bulbs carefully annealed before and after having been filled with mercury, values of κ up to 218° were obtained which are in close agreement with the foregoing. The bulbs were all filled by boiling the mercury in them. This mercury and that used in the gauges was redistilled in the laboratory.

The capillary leading from the air thermometer was as fine as possible, and special care was taken to obtain accurately the temperature of the air in the exposed stem of the thermometer.

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* Proc. Amer. Acad., xv. 98 (1880).

Boiling Point Apparatus.

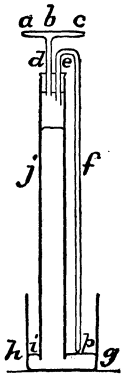
Upon a horizontal circular brass disk of 18 cm. diameter was brazed, with a heavy collar, a vertical thin brass tube 7.8 cm. diameter and 37 cm. high. Eccentrically within this stood a similar tube 6.5 cm. diameter and 34 cm. high, being held in place simply by its weight and by a thin brass collar so near the bottom as to be beneath the surface of the liquid when boiling. Notches cut into the lower edge of the inner tube allowed the vapor formed under this collar to pass into the inner, not into the outer space. A vertical brass tube, open at both ends, about 100 cm. long and 2 cm. diameter, passed through the cover at one side, and extended (by a removable portion) in the outer space of the boiler nearly to the surface of the liquid. This served as an escape and condenser tube, and to its top was attached the exhaustion tube when pressures other than the atmospheric were desired. Outside this a glass condenser was placed for water circulation when benzol was used; with naphthaline and benzophenone this outer jacket was removed. The height to which the vapor extended in the tube could be ascertained by passing a moist cloth along it, and could be readily maintained nearly constant by adjusting the gas flame beneath the boiler. The cover was a brass casting turned and ground to fit a brass ring brazed to the top of the outer tube of the boiler. It was secured to the ring by six screws, and the joint was always very nearly vapor-tight. Through the top were four borings; one nearly central to admit the stem of the air thermometer, three for the insertion of mercurial thermometers to be compared with the air thermometer. These borings were closed by perforated screw-plugs, of which the central one was split lengthwise so that it could be placed on the air thermometer stem after this had been passed through the larger hole in the cover. Leakage was reduced to a minimum by an asbestos packing. Thus, when the liquid was boiling, the circulation of vapor was up the inside tube, in which the mercurial and air bulbs were located, down the jacketing space between the tubes, and up into the condenser tube until liquefied, whence it would drip back into the boiler. The depth of liquid in the boiler was from 2 to 5 cm. The sides and top of the boiler were covered with hair felt from one to three inches thick.

The whole instrument was mounted upon a strong wooden frame in such a way that the cover of the boiler, having the air thermometer rigidly attached to it by a brass bracket, was fixed in place, while the boiler was removable.

For testing mercurial thermometers in the vapor of substances boiling at high temperatures, the following apparatus has been employed. It is similar to the boiler of the larger apparatus. Into the bottom of a thin brass tube, of about 5.3 cm. diameter and 20 cm. high, is brazed a thicker plate. Within this tube stands a shorter tube of about 4.5 cm. diameter notched at the bottom edge, and having a somewhat eccentric collar at about 2 cm. from the bottom, to hold it in place and prevent the vapor from freely rising into the outer jacket. The cover fits with a flange into the top of the outer tube and is split along a diameter. The boring for the insertion of the thermometer is in the centre. Through one half of the cover passes a thin tube about 60 cm. long and 1 cm. internal diameter, projecting about 15 cm. below the cover. This lower portion thus extends nearly to the surface of the liquid in the outer jacket, being placed of course in the larger side of that jacket, and serves as an escape or condenser tube.

Pressure Regulator.

This has been elsewhere described in full,* and is shown in the figure. A Richards water-jet aspirator drew air from *a b c*, and *c* was connected with the apparatus to be exhausted. The small glass tube *e f p* was drawn out to an open point at *p*. As the exhaustion proceeded, the mercury rose in the larger glass tube *j* and in *f*, until the level in the open cistern *h g* fell below *p*, whereupon the mercury in *f* would flow over into *j*, followed by a sudden inrush of air, thus increasing the internal air pressure and causing the mercury to fall somewhat in *j* and rise at *h g*, thus closing *p*. Repetitions of this process would occur until a steady condition was reached, when a nearly regular stream of air and mercury globules would flow continuously through *f*. To maintain steady action, proper relative sizes of tubes and openings must be discovered, and some constriction should be placed in *i j*, and a vessel of large capacity should be present in the circuit. The amount of exhaustion can of course be regulated by the quantity of mercury in the cistern, and by the lengths of the tubes. The pressures were of course measured by a separate mercury column and the barometer.



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* Proc. Amer. Acad, xxi. 1 (1885); Technology Quarterly, i. (1886).

Instrumental Errors.

The barometer was one which had been compared directly with another which had been studied somewhat by a cathetometer, and by comparison with a Signal Service standard in Boston. Its constant error must have been reduced to a fraction of a millimeter, which, so far as it is constant, would not sensibly affect the temperature measurements. Scales were by Brown and Sharpe, of Providence, R. I., and had no errors sensible in this work as compared with a standard scale by Prof. William A. Rogers. Thermometers used were corrected. Those for the more exact work were by Baudin of Paris, and were read to fiftieths of a degree. Pernet's method of thermometry was employed. Calibration and steam exposure corrections were applied. A more extended discussion than has been published, so far as we are aware, as to the precision necessary in the component measurements entering into the air thermometry, was made with a view to best proportioning of parts and their elimination of determinate constant errors.

Preparation of Substances.

This was done by Mr. Gleason, under the direction of Prof. L. M. Norton and Mr. C. W. Andrews of the Chemical Department of the Institute.

Naphthaline. — The pure product from Kahlbaum, of Berlin, was used without subsequent treatment. Samples were fractionated, and all distilled within 0°.3. These distillates were kept separate, each being divided into as many parts as there were tenths rise in temperature, and the melting points of all were found the same. The range of melting and solidifying points of the naphthaline, as taken from the original package, was 79°.38 to 79°.68; after use through the entire series of observations in the boiling-point apparatus it was 79°.42 to 79°.84.

Benzophenone. — The method of Friedel, Crafts, and Ador * was at first selected, on account of its apparent simplicity and the ease of production of considerable quantities of the substance in the pure state. For reasons not known, the rate of production was too small; and the process was abandoned in favor of that of Chancel,† namely, the dry distillation of benzoate of calcium. The benzoate was prepared by neutralizing an aqueous solution of benzoic acid with milk of lime.

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* Comptes Rendus, xxxv. 673.

† Liebig's Ann. d. Chemie u. Pharm., lxxii. 279; lxxx. 285.

When litmus paper gave the neutral reaction, the liquid was filtered hot, evaporated, crystallized, and dried, the mother liquor being evaporated to dryness, and the salt dried. This gave a white product with very little loss. 2500 grams of calcium benzoate were subject to dry distillation, and 820 grams of the crude product were obtained. This liquid was of a dark red color, and 608 grams of it boiled above 200°. The result of fractionation was a straw-colored liquid, which would not solidify by cooling even to —15° C.; but on the addition of a very minute crystal of benzophenone the whole solidified suddenly. This product was again fractionated, and all below 280° rejected. After three recrystallizations from a mixture of alcohol and ether, 500 grams of pure benzophenone were obtained, which, after being dried, melted at 46°.74 to 47°.72; a recrystallization gave the same; but after carrying the benzophenone through the entire series of observations in the boiling-point apparatus, the melting point was 47°.62 to 48°.02, and it solidified at 47°.7, indicating that the initial melting points were probably lowered by presence of alcohol or ether.

Benzol. — The Kahlbaum product was tested for thiophene with isatine, and was shaken with P_2O_5 and distilled. This product melted at 4°.22, and was used in the measurements.

Results.

The direct results obtained will be now given, with deduced formulæ and tables. On page 247 is a table interpolated for each 2 cm. pressure for each substance. In the interpolation for these an application of the method of residual curves greatly facilitated the work. Each table of observations contains two or more series. Columns headed p give measured pressures in millimeters within the boiler; those headed t give the corresponding temperatures measured by the air thermometer. The correction to reduce the air thermometer to absolute scale is beyond the limits of accuracy of this work, and has therefore been omitted.

Naphthaline.

OBSERVED PRESSURES AND TEMPERATURES.

p.	t.	p.	t.
mm.	°	mm	°
759.8	218.11	84.8	141.94
762.7	218.29	141.4	155.57
713.3	215.20	234.8	172.12
655.9	211.59	336.1	184.83
555.7	204.61	461.0	197.02
454.4	196.34	546.7	203.91
352.2	186.39	638.1	210.31
242.5	172.75	711.0	215.00
130.2	152.38	759.0	217.84

Within the limits of 730 and 760 mm. the temperature varies almost directly as the pressure, so that the expression

$$t^\circ = 218.07 + 0.0625\,(H - 760),$$

serves to give the boiling point of naphthaline under any ordinary atmospheric pressure, H, expressed in normal millimeters of mercury. This and subsequent similar ones may probably be used safely up to 780 mm. The following table serves to compare our results with those of Crafts.

p.	t, Crafts.	t, H. and G.
mm.	°	°
720.39	215.7	215.60
730.31	216.3	216.21
740.35	216.9	216.84
750.50	217.5	217.48
760.74	218.1	218.12

[N. B. — In Crafts's original tables appear the erroneous values 753.90 - 217°.8, 755.31 - 217°.9. These pressures should be about 755.60 and 757.31, respectively, as inspection will show.]

Benzophenone.

OBSERVED PRESSURES AND TEMPERATURES.

p.	t.	p.	t.
mm.	°	mm.	°
755.1	305.34	104.3	223.60
698.1	301.69	220.2	251.92
644.1	298.08	314.3	265.56
527.7	288.61	445.2	280.93
432.5	280.14	580.5	292.56
318.1	266.52	660.0	299.19
201.2	250.58	739.9	304.76
88.9	219.59	....	....

COMPARISON WITH CRAFTS'S RESULTS.

Press.	Crafts.	H. and G.
mm.	°	°
732.38	304.3	303.94
740.06	304.8	303.41
750.91	305.5	305.05
760.32	306.1	305.62

Between 720 and 760 mm. the following expression applies to express boiling point as a function of vapor pressure: —

$$t^\circ = 305.6 + 0.060\ (H - 760).$$

Benzol.

OBSERVED PRESSURES AND TEMPERATURES.

p.	t.	p.	t.
mm.	°	mm.	°
769.8	80.65	400.7	60.57
733.6	78.71	351.7	57.34
698.7	77.43	352.9	57.63
660.1	75.70	448.8	63.90
608.8	73.11	589.9	72.13
554.7	70.42	652.5	75.52
518.8	68.54	730.1	79.09
454.6	64.78	768.8	80.57

Between 720 and 780 mm. the following expression applies: —

$$t^\circ = 80.19 + 0.0455\ (H - 760).$$

BOILING POINTS FROM 8 CM. TO 76 CM.

Press.	Naphthaline.	Benzophenone.	Benzol.	Press.	Naphthaline.	Benzophenone.	Benzol.
p.	t.	t.	t.	p.	t.	t.	t.
cm.	°	°	°	cm.	°	°	°
8	140 84	216.0	....	44	195.07	280.4	63.57
10	145.84	222.8	....	46	196.89	282.4	64.90
12	150.54	229.2	....	48	198.59	284.3	66.20
14	154.86	235.0	....	50	200.24	286.2	67.42
16	158.70	240.4	....	52	201.85	287.9	68.58
18	162.48	245.1	....	54	203.40	289.7	69.66
20	166.10	249.1	....	56	204.92	291.5	70.70
22	169.46	252.6	....	58	206.42	293.2	71.70
24	172.67	255.8	....	60	207.88	294.8	72.66
26	175.48	258.7	....	62	209.30	296.4	73.64
28	178.10	261.4	....	64	210.63	297.8	74.60
30	180.58	264.0	....	66	211.86	299.2	75.57
32	182.93	266.6	....	68	213.10	300.5	76.53
34	185.17	269.1	....	70	214.35	301.8	77.47
36	187.28	271.6	58.00	72	215.58	303.1	78.37
38	189.32	273.9	59.40	74	216.80	304.4	79.28
40	191.29	276.1	60.77	76	218.07	305.6	80.19
42	193.20	278.3	62.17	78	....	....	81.10

This investigation constituted the thesis work of Mr. Gleason, and the experimental work was very largely conducted by him alone. The expense attending the work has been met in part by an appropriation from the Rumford Fund of the American Academy of Arts and Sciences, in part by the Institute.

Rogers Laboratory of Physics,
August, 1887.